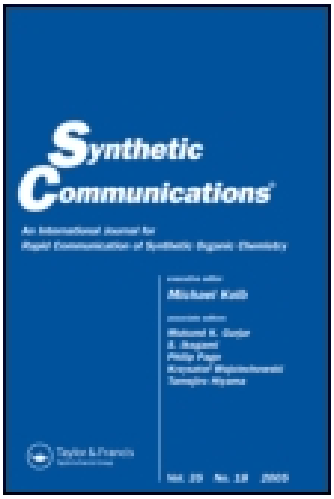

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

One-Step Conversion of Acetophenones to α-Haloacetophenone Dimethyl Acetals Using DCDMH/DBDMH and Molecular Sieve in Methanol

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Accepted author version posted online: 21 Oct 2011.Published online: 25 Jan 2012.

To cite this article: Bin Zhou, Zizhan Chen, Zubiao Zheng, Bingbing Han & Xinzhuo Zou (2012) One-Step Conversion of Acetophenones to α-Haloacetophenone Dimethyl Acetals Using DCDMH/DBDMH and Molecular Sieve in Methanol, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:10, 1445-1453, DOI: 10.1080/00397911.2010.540696

To link to this article: http://dx.doi.org/10.1080/00397911.2010.540696

Synthetic Communications®, 42: 1445–1453, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.540696

ONE-STEP CONVERSION OF ACETOPHENONES TO α-HALOACETOPHENONE DIMETHYL ACETALS USING DCDMH/DBDMH AND MOLECULAR SIEVE IN METHANOL

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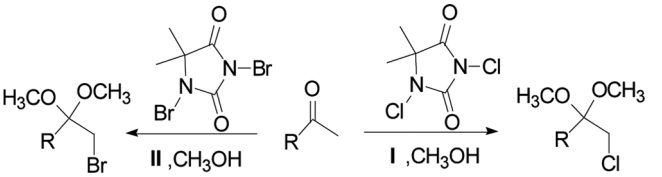
GRAPHICAL ABSTRACT



Abstract *Using DCDMH/DBDMH as* N*-halo reagent, piperidine as catalyst, and 4-A molecular sieve as water-removing agent, α-haloacetophenone dimethyl acetals were directly obtained from the solvent of methanol. As to the substrates with electron-withdrawing groups, the conversions were 80–100%.*

Keywords Acetophenone; 1,3-dibromo-5,5-dimethylhydantoin; 1,3-dichloro-5,5-dimethylhydantoin; α-haloacetophenone dimethyl acetals; molecular sieve; one-step conversion; piperidine

INTRODUCTION

Halogenated organic compounds have received much attention because they can be easily converted into other functional molecules as synthetic intermediates and precursors.[1] Recently, many research papers with wonderful results focus on the formation of acetophenone dimethyl acetals.[2] α-Haloacetophenone dimethyl acetals are a kind of halogentated molecules with acetal structure, and they constitute an interesting class of synthetic intermediates that can be used to prepare novel flavor material and other sorts of functional compounds.[3] However, as to the preparation of α-haloacetophenone dimethyl acetals, the reports are rare.[4]

Both 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) are disinfecting agents and bleaching agents that

Received September 10, 2010.

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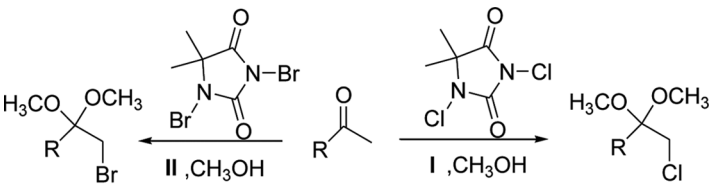
have been extensively used in industrial and domestic water and fruit storage.[5] Application of DCDMH or DBDMH in some aspects has been widely researched, and some methods about DCDMH or DBDMH have been described by our group.[6] α-Chloroacetophenone dimethyl acetals were found as by-products when DCDMH was refluxed with acetophenones and methanol during our research.[6c] Generally speaking, there is a chemical equilibrium between ketones and ketals. Acids are used as catalysts to prepare ketals from ketones, and trimethyl orthoformate is widely used to prepare acetophenone dimethyl acetals.[7] Additionally, if α-haloacetophenone dimethyl acetals need to be prepared from acetophenones, there are two steps to reach the target molecules, halogenation and acetalization. In our research, the α-haloacetophenone dimethyl acetals as by-products were obtained without trimethyl orthoformate and acids in just one step so we decided to develop and optimize a method for preparation of α-haloacetophenone dimethyl acetals based on our findings (Scheme 1).

First, *p*-nitroacetophenone **1a** was chosen as a model for the reaction of α-chlorination and acetalization in one step. Various amounts of DCDMH were tested, and 2 equiv. of DCDMH were beneficial to the reaction. Compound **1a** was treated with 2 equiv. of DCDMH in the presence of silica gel (1 g) and CH_3OH under reflux by various catalysts. The amount of catalyst was 10 mmol, and the results were shown in Table 1. When Et_3N was used as catalyst, only 65% of substrate was converted into the corresponding product **2a** and the remaining of **1a** was transformed into the α-chloro-4-nitroacetophenone. Only trace of α,α-dichloro-4-nitroacetophenone was found, which was determined by ^1H NMR (Table 1, entry 1). When the reaction was catalyzed by pyridine, Et_2NH, or 1-butylamine, the conversions to α-chloro-4-nitroacetophenone dimethyl acetals were 74%, 80%, and 84% (Table 1, entries 2–4). As to piperidine, the conversion reached 89%, the highest among our experimental results (Table 1, entry 5). We thought piperidine was helpful to this reaction in that the substrate was α-chlorinated and acetalizated in one step. Molecular sieve (4A) replaced silica gel as water-removing agent, and interestingly the conversion increased to 100%. The 4A moleculor sieve can be reused during our experiments. Because **1a** was very reactive, **1d** with mild reactivity was selected to be the tested compound to optimize the amount of the amine. Compound **1d** was heated with 4A molecular



1a: R=*p*-nitrophenyl
1b: R=*m*-nitrophenyl
1c: R=*p*-trifluoromethylphenyl
1d: R=*p*-bromophenyl
1e: R=*p*-chlorophenyl
1f: R=*o*-chlorophenyl
1g: R=2,4-dichlorophenyl
1h: R=3,4-dichlorophenyl
1i: R=phenyl
1j: R=*p*-methylphenyl

Scheme 1. One-step conversion of acetophenones to α-haloacetophenone dimethyl acetals using DCDMH/DBDMH and molecular sieve in methanol. **I**: piperidine, 4-sieves, MeOH, reflux, 12 h. Conversions: 50–100%. **II**: piperidine, 4-A sieves, MeOH, 50–52°C, 12h. Conversions: 50–100%.

Table 1. Conversion of **1a** catalyzed by various amines[a]

Entry	Catalyst	Conversion (%)[b]
1	Et_3N	65
2	Pyridine	74
3	Et_2NH	80
4	1-Butylamine	84
5	Piperidine	89

[a]**1a** (10 mmol), DCDMH (20 mmol), silica gel (1 g), MeOH 35 mL, reflux for 12 h.

[b]The conversion to **2a** was determined by ^{1}H NMR analysis of the crude reaction mixture.

sieves, and 10, 5, 2.5, 1, or 0 mmol of piperidine were added to the reaction mixture. The conversions of **1d** were from 81% to 92%, and the conversion that used 2.5 mmol piperidine was 92%, higher than the other experimental results.

Various acetophenones were examined, and the substrates were heated with 2 equiv. of DCDMH, 2.5 mmol piperidine, and 15 g 4A molecular sieve in MeOH at reflux for 12 h. We found the chemical conversions of most of substrates were high, and most of the substrates could be converted to the corresponding products in good yield. The conversions of **1a**–**1h** were 92–100%, and the isolated yields of **2a**–**2h** were from 82% to 94% (Table 2, entries 1–8). In the mixture of the crude products of **1j**, 25% of α,α-dichloro-*p*-methylacetophenone was found by ^{1}H NMR (Table 2, entry 10). The conversion and isolated yield of **1i** were respectively 86% and 72% (Table 2, entry 9). In our new chemical process of α-chlorination and acetalization in one pot, the substrates with electron-withdrawing groups seem to offer products with good yields, and the yields of the substrates with electron-donating groups were less than the substrates with electron-withdrawing groups.

When DBDMH was used instead of DCDMH and other conditions remained, some α,α-dibromoacetophenones were found. We adjusted the temperature to 50–52°C, and the α,α-dibromoacetophenones almost disappeared; the conversion of the tested substrate **1f** was 86%. When the reaction was carried out at room temperature, the product was not detected. Various substrates were tested, and the substrates were mixed with 2 equiv. of DBDMH, 2.5 mmol piperidine, and 15 g 4A moleculor sieve in MeOH at 50–52°C for 12h. The conversions of **1a**–**1h** were 70–100%, and the isolated yields of **3a**–**3h** were from 62% to 93% (Table 2, entries 1–8). The yields of **3i** were 38%, which was lower than **3a**–**3h** (Table 2, entry 9). As to the substrate **1j**, the conversion of **1j** was very low (< 1%) (Table 2, entry 10). In the process of α-bromination and acetalization in one pot, the substrates with electron-withdrawing groups could also offer products with good yields. On the whole, the yields of the substrates in the process of α-chlorination and acetalization were greater than those in the process of α-bromination and acetalization.

Xu et al. gave the mechanism about keto-enol tautomerism in the process of the bromination of substituted acetophenones using DCDMH in the presence of *p*-TsOH (see Ref. [6a] and references therein). Analogously, we propose the following mechanism (Scheme 2) for the reaction, in which piperidine was used as a catalyst and 4A molecular sieves were used in methanol. In this reaction, DCDMH/DBDMH

Table 2. α-Halogenation and acetalization of various acetophenones in one step

Entry	Substrate	Conversion (%)[c]	
		2[a]	**3**[b]
1	**1a**	100 (94)	100 (93)
2	**1b**	100 (91)	98 (92)
3	**1c**	100 (87)	80 (70)
4	**1d**	92 (82)	70 (62)
5	**1e**	98 (85)	77 (68)
6	**1f**	100 (85)	86 (79)
7	**1g**	100 (86)	89 (84)
8	**1h**	100 (85)	89 (84)
9	**1i**	86 (72)	50[e] (38)
10	**1j**	50[d] (40)	<1 (Trace)

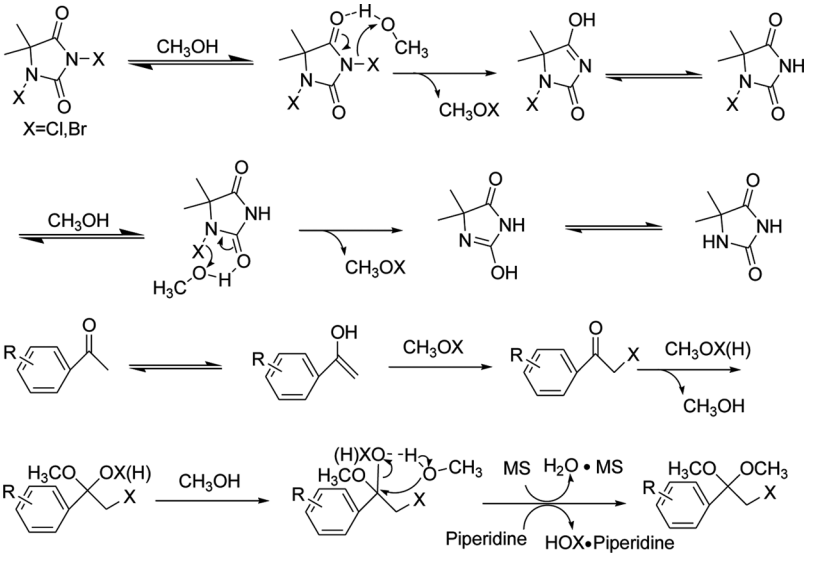
[a]Substrate (10 mmol), DCDMH (20 mmol), 4-A molecular sieves (15 g), piperidine (2.5 mmol), MeOH (35 mL), reflux for 12 h.

[b]DBDMH (20 mmol) and the reaction mixture was heated to 50–52°C for 12 h.

[c]The conversion to α-haloacetophenone dimethyl acetals was determined by ^{1}H NMR analysis of the crude reaction mixture. The isolated yields were in the brackets.

[d]**2j**, α-chloro-*p*-methyl-acetophenone and α,α-dichloro-*p*-methylacetophenone were found in the products and the ratio of the three compounds determined by ^{1}H NMR was 2:1:1.

[e]7% of the α,α-dichloroacetophenone was also found in the products determined by ^{1}H NMR.



Scheme 2. Possible mechanism for one-step conversion of acetophenones to α-haloacetophenone dimethyl acetals using DCDMH/DBDMH and molecular sieve in methanol.

could emit Cl^+ or Br^+ twice, so maybe CH_3OCl or CH_3OBr was helpful to the process and CH_3OCl or CH_3OBr was involved in not only α-halogenation but also acetalization. Piperidine and molecular sieves played an important role in the reaction respectively as acid and water-removing agent.

In conclusion, we developed a simple and efficient method to prepare α-haloacetophenone dimethyl acetals directly from acetophenones in one pot in mild conditions. The method to prepare an important and interesting class of synthetic intermediates is combined with two reactions (α-halogenation and acetalization) in a one-step process with some cheap and clean reagents such as DCDMH and DBDMH. The method is a novel route to α-haloacetophenone dimethyl acetals in the methodology of organic synthesis.

EXPERIMENTAL

Typical Experimental Procedure of α-Halogenation and Acetalization

Piperidine (2.5 mmol) and 4A molecular sieves (15 g) were added into a mixture of substrate (10 mmol), DCDMH/DBDMH (20 mmol), and methanol (35 mL). After reflux for 12 h (or heating to 50–52 °C when DBDMH was used), the mixture was filtered, and the solvent of methanol was removed from the filtrate under reduced press. After MTBE (50 mL) was added to the residue, the organic layer was washed by water (40 mL) and brine (50 mL) several times, and the organic layer was dried on Na_2SO_4. After that, the organic layer was filtered, and the solvent was removed under reduced pressure. The product was obtained.

1-(2-Chloro-1,1-dimethoxyethyl)-4-nitrobenzene (2a)

Light yellow solid; mp 48–49°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.23 (d, 2H, $J = 8.6$ Hz, Ar-H), 7.70 (d, 2H, $J = 8.6$ Hz, Ar-H), 3.73 (s, 2H, -CH_2), 3.24 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 148.1, 145.5, 128.6, 123.2, 101.5, 49.4, 45.9; *m/z*: 214, 196, 150; IR (KBr, cm^{-1}): 1528, 1352, 1287, 1126, 1073, 1053. EA calculated for $C_{10}H_{12}NO_4Cl$: C, 48.89%; H, 4.92%; N, 5.70%, found: C, 48.85%; H, 5.12%; N, 5.72%.

1-(2-Chloro-1,1-dimethoxyethyl)-3-nitrobenzene (2b)

Light yellow solid; mp 51–52°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.39 (s, 1H, Ar-H), 8.22–8.24 (m, 1H, Ar-H), 7.84–7.86 (m, 1H, Ar-H), 7.58–7.60 (m, 1H, Ar-H), 3.74 (s, 2H, -CH_2), 3.26 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 148.3, 140.8, 133.4, 129.1, 123.5, 122.8, 101.3, 49.4, 45.9; *m/z*: 214, 196, 150; IR (KBr, cm^{-1}): 1530, 1350, 1127, 1097, 1073, 1054. EA calculated for $C_{10}H_{12}NO_4Cl$: C, 48.89%; H, 4.92%; N, 5.70%, found: C, 48.95%; H 5.04%; N 5.71%.

1-(2-Chloro-1,1-dimethoxyethyl)-4-trifluoromethylbenzene (2c)

Light yellow oil;^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.64 (s, 4H, Ar-H), 3.74 (s, 2H, -CH_2), 3.24 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.4, 130.4, 127.9. 125.0, 125.0, 101.5, 49.3, 46.1; *m/z*: 237, 219, 173; IR (KBr, cm^{-1}): 1384, 1125, 1075, 1002.

1-Bromo-4-(2-chloro-1,1-dimethoxyethyl)benzene (2d)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.49 (d, 2H, $J = 7.8$ Hz, Ar-H), 7.37 (d, 2H, $J = 7.8$ Hz, Ar-H), 3.70 (s, 2H, -CH_2), 3.22 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 138.8, 132.6, 132.3, 130.0, 129.7, 126.6, 101.1, 49.3, 46.0; *m/z*: 249, 229, 183; IR (KBr, cm^{-1}): 1124, 1073, 1051, 1011.

1-Chloro-4-(2-chloro-1,1-dimethoxyethyl)benzene (2e)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.45 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.36 (d, 2H, $J = 8.4$ Hz, Ar-H), 3.70 (s, 2H, -CH_2), 3.21 (s, 6H, -OCH_3).[8]

1-Chloro-2-(2-chloro-1,1-dimethoxyethyl)benzene (2f)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.86–7.88 (m, 1H, Ar-H), 7.38–7.40 (m, 1H, Ar-H), 7.28–7.30 (m, 2H, Ar-H), 3.84 (s, 2H, -CH_2), 3.23 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 134.4, 132.3, 131.1, 131.0, 129.8, 126.4, 101.1, 48.8, 42.7; *m/z*: 203, 185, 139; IR (KBr, cm^{-1}): 1384, 1127, 1082, 1063, 1002.

2,4-Dichloro-1-(2-chloro-1,1-dimethoxyethyl)benzene (2g)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.80 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.40 (s, 1H, Ar-H), 7.29 (d, 1H, $J = 8.5$ Hz, Ar-H), 3.93 (s, 2H, -CH_2), 3.23 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 135.1, 133.4, 132.0, 130.6, 130.6, 126.7, 101.0, 48.9, 42.5; *m/z*: 237, 219, 173; IR (KBr, cm^{-1}): 1383, 1125, 1081, 1059, 1002, 984.

1,2-Dichloro-4-(2-chloro-1,1-dimethoxyethyl)benzene (2h)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.62 (s, 1H, Ar-H), 7.46 (d, 1H, $J = 8.4$ Hz, Ar-H), 7.33 (d, 1H, $J = 8.4$ Hz, Ar-H), 3.69 (s, 2H, -CH_2), 3.22 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 137.4, 131.1, 129.1, 122.6, 101.6, 49.1, 46.2; *m/z*: 237, 219, 173; IR (KBr, cm^{-1}): 1290, 1121, 1076, 1055.

(2-Chloro-1,1-dimethoxyethyl)benzene (2i)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.51–7.53 (m, 2H, Ar-H), 7.38–7.40 (m, 3H, Ar-H), 3.75 (s, 2H, -CH_2), 3.24 (s, 6H, -OCH_3).[9]

1-(2-Chloro-1,1-dimethoxyethyl)-4-methylbenzene (2j)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.42 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.24 (d, 2H, $J = 8.4$ Hz, Ar-H), 3.70 (s, 2H, -CH_2), 3.21 (s, 6H, -OCH_3), 2.54 (s, 3H, -CH_3).[10]

1-(2-Bromo-1,1-dimethoxyethyl)-4-nitrobenzene (3a)

Light yellow solid; mp 49–50°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.25 (d, 2H, $J = 9$ Hz, Ar-H), 7.71 (d, 2H, $J = 9$ Hz, Ar-H), 3.62 (s, 2H, -CH_2), 3.25 (s,

6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 148.0, 145.7, 128.5, 123.2, 101.0, 49.6, 34.5; *m/z*: 258, 196, 150; IR (KBr, cm^{-1}): 1522, 1352, 1282, 1114, 1047. EA calc. for $C_{10}H_{12}NO_4Br$: C, 41.40%; N, 4.83%; H, 4.17%, found: C, 41.45%; N, 4.81%; H, 4.15%.

1-(2-Bromo-1,1-dimethoxy-ethyl)-3-nitrobenzene (3b)

Light yellow solid; mp 68–69°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 8.38 (s, 1H, Ar-H), 8.19–8.21 (m, 1H, Ar-H), 7.82–7.84 (m, 1H, Ar-H), 7.58–7.60 (m, 1H, Ar-H), 3.62 (s, 2H, -CH_2), 3.25 (s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 148,3, 141.1, 133.4, 129.1, 123.5, 122.8, 100.8, 49.6, 34.7; *m/z*: 258, 196, 150; IR (KBr, cm^{-1}): 1529, 1350, 1271, 1121, 1089, 1043. EA calc. for $C_{10}H_{12}NO_4Br$: C, 41.40%; N, 4.83%; H, 4.17%, found: C, 41.47%; N, 4.83%; H, 4.27%.

1-(2-Bromo-1,1-dimethoxyethyl)-4-trifluoromethylbenzene (3c)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.55 (s, 4H, Ar-H), 3.53 (s, 2H, -CH_2), 3.15 (s, 6H, -OCH_3);^{13}C NMR (125 MHz, $CDCl_3$): δ: 142.6, 130.2, 127.8, 125.0, 124.9, 101.0, 49.4, 34.9; *m/z*: 281, 219, 173; IR (KBr, cm^{-1}): 1326, 1166, 1127,1068, 1049.

1-Bromo-4-(2-bromo-1,1-dimethoxyethyl)benzene (3d)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.52 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.39 (d, 1H, $J = 8.5$ Hz, Ar-H), 3.60 (s, 2H, -CH_2), 3.21 (s, 6H, -OCH_3);^{13}C NMR (125 MHz, $CDCl_3$): δ: 137.7, 131.1, 129.1, 122.7, 101.1, 49.4, 35.1; *m/z*: 293, 229, 183; IR (KBr, cm^{-1}): 1282, 1108, 1065, 1043, 1008.

1-(2-Bromo-1,1-dimethoxyethyl)-4-chlorobenzene (3e)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.46 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.37 (d, 2H, $J = 8.4$ Hz, Ar-H), 3.60 (s, 2H, -CH_2), 3.23 (s, 6H, -OCH_3).[11]

1-(2-Bromo-1,1-dimethoxyethyl)-2-chlorobenzene (3f)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.83–7.85 (m, 1H, Ar-H), 7.35–7.37 (m, 1H, Ar-H), 7.27–7.29 (m, 2H, Ar-H), 3.94 (s, 2H, -CH_2), 3.23 (s, 6H, -OCH_3);^{13}C NMR (125 MHz, $CDCl_3$): δ: 134.7, 132.4, 131.3, 131.1, 130.1, 126.3, 100.7, 49.1, 31.6; *m/z*: 249, 185, 139; IR (KBr, cm^{-1}): 1116, 1074, 1059, 1041.

1-(2-Bromo-1,1-dimethoxyethyl)-2,4-dichlorobenzene (3g)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.78 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.39 (s, 1H, Ar-H), 7.27 (d, 1H, $J = 8.5$ Hz, Ar-H), 3.88 (s, 2H, -CH_2), 3.21 (s, 6H, -OCH_3).[12]

4-(2-Bromo-1,1-dimethoxyethyl)-1,2-dichlorobenzene (3h)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 7.61 (s, 1H, Ar-H), 7.43 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.31 (d, 1H, $J = 8.5$ Hz, Ar-H), 3.56 (s, 2H, -CH_2), 3.21

(s, 6H, -OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ: 139.0, 132.6, 132.3, 130.0, 129.7, 126.6, 100.6, 49.4, 34.7; *m/z*: 283, 219, 173; IR (KBr, cm^{-1}): 1117, 1069, 1047, 1026.

(2-Bromo-1,1-dimethoxyethyl)benzene (3i)

Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$): δ: 7.57–7.59 (m, 2H, Ar-H), 7.34–7.36 (m, 3H, Ar-H), 3.62 (s, 2H, -CH_2), 3.22 (s, 6H, -OCH_3).[10]

ACKNOWLEDGMENT

The authors thank Shanghai Foundation of Science and Technology for finacial support (No. 073919106).

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